

Final Report for Period: 10/2010 - 09/2011**Submitted on:** 02/06/2012**Principal Investigator:** Huey, L. G.**Award ID:** 0612387**Organization:** Georgia Tech Research Corp**Submitted By:**

Huey, L. - Principal Investigator

Title:

Collaborative Research: Radical Chemistry over Sunlit Snow at Summit, Greenland

Project Participants**Senior Personnel****Name:** Huey, L.**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Tanner, David**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Brough, Neil**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Deploying to Summit to help obtain field data

Post-doc**Graduate Student****Name:** Liao, Jin**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Data analysis and deployment to Greenland

Undergraduate Student**Name:** Cummings, Anthony**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Performed as member of field team. Helped analyze data, maintain instruments, take down and ship back to U.S. Supported by this proposal.

Name: Reichardt, Helen**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Performed as member of field team. Helped analyze data, maintain instruments, take down and ship back to U.S. Supported by this proposal.

Technician, Programmer**Other Participant**

Research Experience for Undergraduates**Organizational Partners****NASA Langley**

Gao Chen is helping with photochemical modeling and data analysis.

British Antarctic Survey

BAS is providing personnel to help run CIMS instrument at Summit. This is a continuation of collaborative research on photochemistry and halogens that Ga. Tech carried out in collaboration with BAS.

Other Collaborators or Contacts**Activities and Findings****Research and Education Activities: (See PDF version submitted by PI at the end of the report)**

In the past year we published a detailed study of the HOx and BrO chemistry based on our observations at Summit, Greenland in ACP. variety of photochemical calculations that include both HONO and halogen chemistry are described and compared to observations. A final paper looking at HOx photochemistry using a 1-d snow model has been submitted to ACPD to finalize the project.

Findings: (See PDF version submitted by PI at the end of the report)

Our measurements of radicals indicate that we understand the overall HOx sources and sinks over the Greenland Ice Sheet. However, the OH partitioning is perturbed from that expected from basic NOx chemistry. The inclusion of BrO observations improves our predictions of OH levels. However, we still find periods when OH levels are higher than we can predict and they are coincident with elevated levels of reactive gaseous mercury. In summary, our general understanding of HOx chemistry and its interaction with BrO is solid but there are a few details that need to be addressed.

Training and Development:

We have two undergrad students (Cummings and Reichardt) who have helped get instruments ready for deployment. They have both gone to twice to Summit, Greenland to help run instruments in the field. They have also done data analysis for our observations. Jin Liao has deployed to the field and performed the data analysis and modeling of the Br and RGM data reported in the findings section. She is the first author of the final ACP paper and she has graduated and accepted a postdoctoral position at NOAA.

Outreach Activities:

There have been no major outreach activities in the current year.

Journal Publications

Liao, J; Huey, LG; Tanner, DJ; Brough, N; Brooks, S; Dibb, JE; Stutz, J; Thomas, JL; Lefer, B; Haman, C; Gorham, K, "Observations of hydroxyl and peroxy radicals and the impact of BrO at Summit, Greenland in 2007 and 2008", ATMOSPHERIC CHEMISTRY AND PHYSICS, p. 8577, vol. 11, (2011). Published, 10.5194/acp-11-8577-201

Books or Other One-time Publications**Web/Internet Site**

Other Specific Products

Contributions

Contributions within Discipline:

We have definitely demonstrated the importance of halogen chemistry over the Greenland Ice Sheet.

Contributions to Other Disciplines:

Contributions to Human Resource Development:

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

Conference Proceedings

Categories for which nothing is reported:

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Other Disciplines

Contributions: To Any Human Resource Development

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering

Any Conference

Draft Annual Report for Period: 10/2007 - 9/2008

Note that each group needs to submit their own version of this report. Much of it can be identical for all versions. I believe that the only thing each PI needs to be sure about entering correctly are the **Project Participants** from their institution who worked on this project.

Organizational Partners

This is probably already in Fastlane from last year, but each of us needs to list all the other collaborating institutes (e.g., my report would not include UNH):

UNH (Dibb)

UC Irvine (Blake)

Oak Ridge Associated Universities (Brooks, careful not to say he is NOAA!!)

UH (Lefer)

UCLA (Stutz)

From here on, I think we should all be able to copy and paste the same blocks right into Fastlane. I am providing first drafts to be discussed and refined over the next two weeks (or less). Recall that ATM asked us to try to get this in by 15 June.

Other Collaborators or Contacts

Roland von Glasow at the University of East Anglia and Gao Chen at NASA Langley Research center are working closely with us. They have the lead on 1-D and 0-D modeling (respectively) of the interactions of HO_x, NO_x, BrO_x, and Hg, based on observations at Summit in 2007 and 2008. Both attended the 2007 data workshop at UCLA.

We are also anticipating significant collaboration with a large number of other investigators in the IPY POLARCAT campaign, integrating our measurements at Summit with additional measurements made at Summit and throughout the Arctic from multiple platforms.

In particular we expect to compare our surface observations to vertical profiles measured above the ice sheet by the DLR Falcon and NASA DC-8 research aircraft, and to the lidar measurements of the boundary layer over the ice sheet measured from the CNRS ATR-42. The French and German aircraft will be based in Kangerlussuaq and definitely plan to devote significant numbers of flight hours to sampling above central Greenland. The NASA DC-8 plans to dedicate portions of 2 flights to sampling above the ice sheet (an overnight trip to Thule from its operational base in Cold Lake, Alberta will allow several hours sampling over Greenland on both legs). Primary contacts for the aircraft are Hans Schlager (Falcon), Kathy Law (ATR-42), and Jack Dibb (DC-8, though it should be noted that Greg Huey also has 2 instruments on this plane).

We also plan to take advantage of the large theory team supporting POLARCAT with meteorological and chemical transport modeling. All forecast and retrospective analyses will be available to us as partners in POLARCAT, and will be useful to assess transport to Summit during any events that we observe.

We are also very excited about the daily O₃ sondes that NOAA ESRL and ARCIONS (coordinated by Anne Thompson and Sam Oltmans) will launch at Summit as part of POLARCAT, and the fluxes of NO_x, O₃, and VOCs that Richard Honrath and Detlev Helmig will measure in their new POLARCAT project that began at Summit in June.

Research and Education Activities

Most of this reporting period was spent analyzing samples and data collected in the 2007 campaign. Quality controlled results from all instruments and sample streams except for the long-path and MAX DOAS systems have been posted to our internal data archive (available to all members of the team) since early 2008. The DOAS data is currently undergoing re-analysis to ensure the quality of the observations. We had a data workshop at UCLA in December, 2007 to share preliminary results, outline collective analyses of the merge dataset required to produce several group manuscripts on the 2007 findings, and plan for the 2008 campaign. Discussions at the workshop revealed that the 2007 data set is very rich, but would have been enhanced by higher temporal resolution sampling of snow (for Hg and soluble ions) and stronger observation constraints on the diurnal behavior of the boundary layer at Summit. We have begun to develop a snow chemistry model to couple to R. von Glasow's 1D atmospheric chemical transport model MISTRA. The snow chemistry model is currently undergoing testing using observations from Summit from 2003 and 2007.

The results of our project have been presented by Gao Chen at the 2007 EGU meeting, Steve Brooks at the 2008 NOAA Earth System Research Lab annual meeting, and Greg Huey at the fall 2007 meeting of the AGU. Jack Dibb will give an overview talk at the 2008 IGAC meeting.

At the time of writing, we have just returned to Summit for our 2008 campaign (3 June - 11 July). Snow sampling has been increased to twice daily for both, ions and mercury (more frequently during events noted by real time instruments). A 15m snow core for Hg is being collected. And we are making our own measurements of micrometeorology (using a tethered sonde, radiosondes, and meteorological sensors on the CU/Swiss 50-m tower) to complement the baseline measurements made by NOAA ESRL on their tower. We are also measuring Hg fluxes over snow continuously. As noted above, we also expect to benefit from the daily ARCIONS soundings and the turbulence measurements being made by Honrath and Helmig. In addition, we are measuring O₃ at 50 m, 2 m, and 15 cm, to complement NOAA observations at 10 m and Helmig's flux measurement (he will also have continuous measurements at 15 m above the snow). All of our systems became operational on 10 June and are currently producing data. We are eagerly anticipating overflights by the POLARCAT aircraft in the first 10 days of July.

Findings

In our first annual report written shortly after the 2007 field season we summarized our preliminary findings as noted below:

- 1) BrO was detected at Summit by both long path DOAS and the low pressure CIMS. Mixing ratios rarely exceeded 3 pptv, but both techniques reported similar values, and a distinct diurnal pattern (sun-synchronous peak) on most days of the campaign.
- 2) Soluble Br⁻ detected by the MC/IC was also above detection limits throughout the campaign, with a diurnal variation from 0.5 – 1.0 pptv up to about 3.0 pptv that was more or less in phase with that of BrO. On 2 days firn air at a depth of 10 cm was sampled, both days the mixing ratios in firn air exceeded those at 1 m above the snow around the time of solar noon, but even in firn air the mixing ratios did not exceed 10 pptv.
- 3) Aerosol bromide was detected in nearly all of the 24 hour filter samples, but the mixing ratios did not exceed 1 pptv. Increasing temperatures in late May and early June appeared correlated with a significant drop in aerosol bromide.
- 4) Mercury showed distinct diurnal changes in speciation that would appear to be consistent with Br chemistry. GEM often decreased at mid-day, while RGM was increasing. Many days the fine particulate Hg peaked in the evening, out of phase with the RGM.
- 5) The HO₂/OH ratio showed a pronounced and repeated daily cycle, with a deep minimum around noon on most days. Model studies to assess whether this pattern is consistent with control by NO_x chemistry, or indicative of Br chemistry, are beginning now.
- 6) NO mixing ratios were lower than we observed in 2003 and 2004 (also lower than those reported by Honrath et al. during the 1998, 1999, and 2000 seasons).

All of these findings have survived closer scrutiny over the past year.

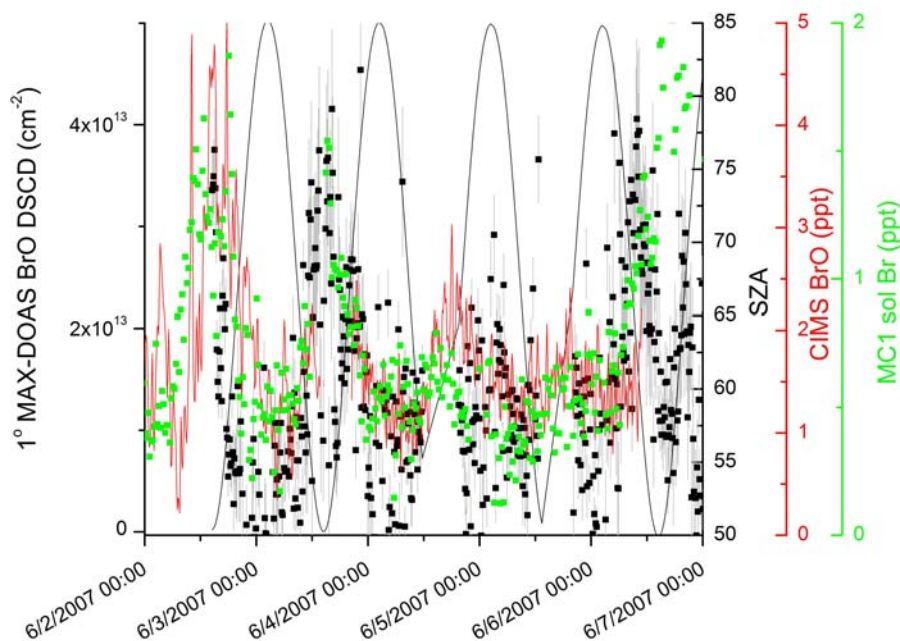


Figure 1: Intercomparison of CIMS BrO mixing ratios (red), MAX-DOAS BrO differential slant column densities (DSCD) (black) and soluble bromide (green).

Figure 1 shows an intercomparison of the various bromine measurements during a five day period. Using a typical airmass factor and boundary layer height to convert the MAX-DOAS DSCD's to boundary layer averaged mixing ratios yields similar results to the CIMS observations. The diurnal pattern in the bromine data is clearly visible.

Preliminary analysis with the 0-D model strongly suggest that the BrO levels are significantly impacting both Hg and HO_x at Summit. As we found in 2003, standard chemistry (not including Br) fails to account for elevated OH observed for periods of hours to several days. In 2007, largest discrepancies between model estimated and observed OH occurred at the same times that RGM was enhanced, and O₃ was modestly depressed (Figure 2). Br is the only oxidant known to be capable of oxidizing GEM to RGM rapidly enough to create the pronounced diurnal variations of RGM we observed. Nighttime minima of RGM suggest that deposition to the snow is a strong sink, and imply an RGM lifetime at Summit during our campaign in the 3-10 hour range. Assuming that a 7-hour lifetime is short enough that RGM production is roughly balanced by deposition allows estimation of Br from the steady state relationship:

$$[\text{Br}] = \frac{[\text{RGM}]}{[\text{GEM}] \cdot k_{\text{Br}+\text{GEM}} \cdot (7\text{hr})}$$

It should be noted that $k_{\text{Br}+\text{GEM}}$ is not well established, determinations reported by *Ariya et al. (2002)* and *Donohoue et al. (2006)* differ by nearly an order of magnitude. Both values were used to estimate Br. The lifetime of BrO at Summit in May-June is on the order of 25 s, allowing BrO to be estimated using the Br constrained by Hg observations and the relationship:

$$\frac{[\text{BrO}]}{[\text{Br}]} = \frac{k_1[\text{O}_3]}{2k_2[\text{BrO}] + k_3[\text{HO}_2] + k_4[\text{NO}] + J_{\text{BrO}}}$$

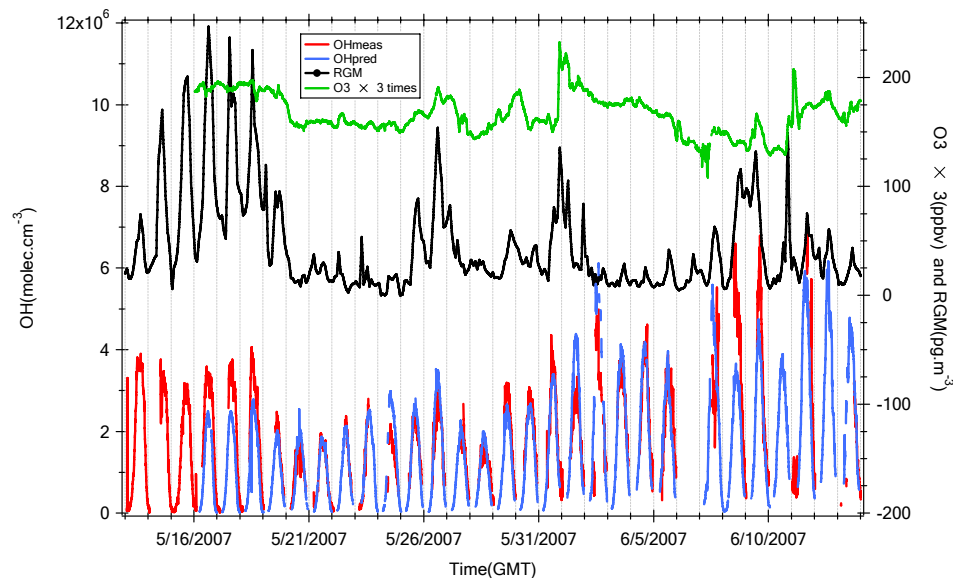


Figure 2. Comparison of OH predictions from the $\text{HO}_x\text{-NO}_x\text{-CH}_4$ model to OH measurements, plotted with RGM and O_3 concentrations.

Adding Br chemistry into the 0-D model, with Br estimated from Hg as described above leads to marked improvement in the comparison between modeled and observed OH (Figure 3), and also yields estimated BrO levels similar to the CIMS observations (Figures 3 and 4) when the *Donohoue et al. (2006)* rate constant is used. Making the same calculation using the *Ariya et al. (2002)* rate constant suggests much lower levels of Br and BrO that have negligible impact on HO_x cycling under the conditions we observed at Summit.

We realize that the steady state assumption for RGM is tenuous, and introduces large uncertainty into the estimation of Br, hence BrO. In the future our 1D model will allow a more quantitative description of bromine and Hg chemistry.

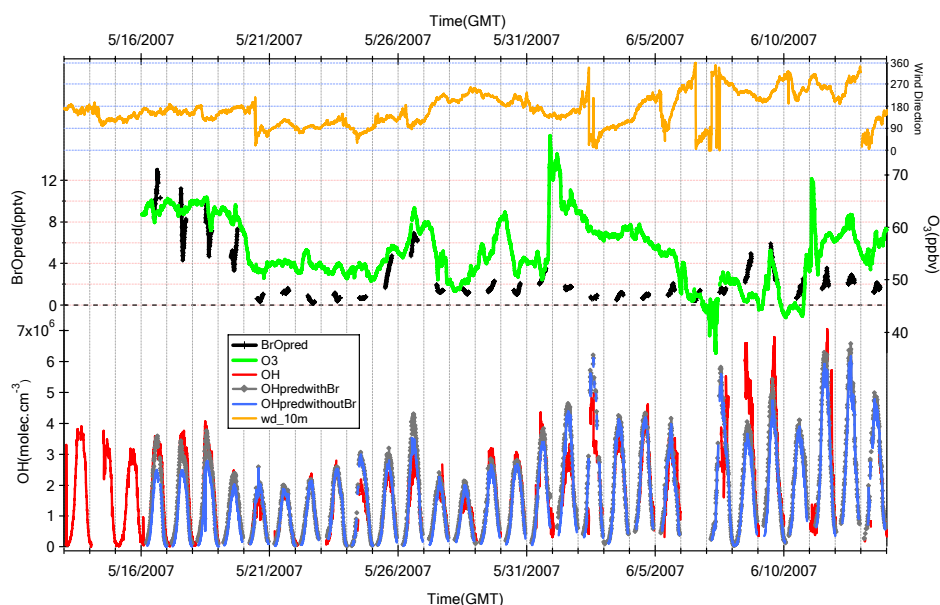


Figure 3. Comparison of OH predictions from the HO_x-NO_x-CH₄-BrO_x model to OH measurements, plotted with BrO_x predictions, ozone and wind direction at 10 m for the rate constant of *Donohoue et al.*.

The combined dataset from the 2007 Summit field campaign indicates that reactive bromine is present at significant levels. Analysis of RGM data with the rate constant for reaction measured by *Donohoue et al.* (2006) and the CIMS observations are consistent with daytime BrO levels of at least 1-2 pptv with periods of up to 5-10 pptv. This is consistent with the persistent low level depletion of ozone in the Summit boundary layer relative to the air above.

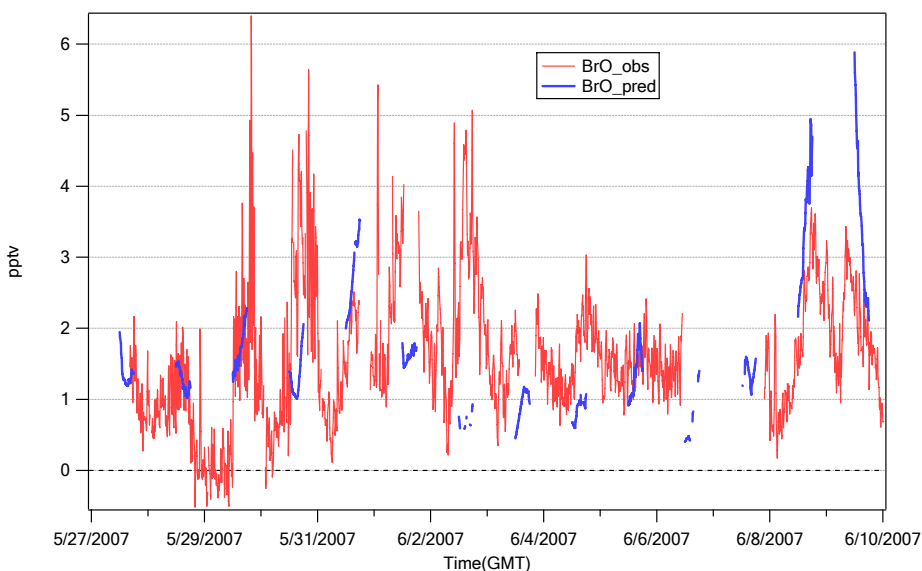


Figure 4. Comparison of the predicted BrO concentrations (using the *Donohoue et al.* rate constant for Br + GEM) and the observed BrO levels.

Training:

Three graduate students (Luke Ziemba, Katrine Gorham, and Mathias Piot) and three undergraduate students (Bonnie Reichardt, Justin Juhan, and Tony Cummings) were active participants in the 2007 field campaign. All of the graduate students have also been involved in data analysis back at their home institutions.

Luke, Katrine, Bonnie and Tony have all returned to Summit in 2008. They have been joined by one more undergraduate student (Max Schneider), 5 more graduate students (Jeff Luxford, Jin Liao, Christine Haman, Chris Moore and Tara Kahan), and a postdoctoral researcher (Jennie Thomas). Jin had planned to participate in 2007 but visa issues prevented that, we note that she has done most of the analysis summarized immediately above.

Outreach:

We are once again hosting a PolarTREC teacher, Mr. Craig Beals. He is currently at Summit with our team. He will host several online web seminars to middle school and high school students in which our scientists and students will participate. The first PolarTREC event is scheduled for June 10. In addition to his PolarTREC activities, Craig will host interactive online presentations to 'at risk' high school students attending an Environmental Science summer program through Montana State University in Billings. The Polarpalooza movies describing our Summer 2007 field activities are now available to a wider audience on Youtube.

Publications

The results of our project have been presented by Gao Chen at the 2007 EGU meeting and Greg Huey at the fall meeting of the AGU. Jack Dibb will give an overview talk at the 2008 IGAC meeting.

Comment [JPS1]: There is little we can do. We can try to enter the talks. Do you have the title of Gao's Talk?

Web site

<http://gshox.blogspot.com>

<http://greenland-2008.blogspot.com>

<http://www.polartrec.com/greenland-atmospheric-studies>

Contributions

...In Discipline

We have confirmed that halogen (at least Br) chemistry is active at Summit, and that it significantly perturbs HO_x and Hg cycling there. We hope that the 2008 measurements and further analysis of the combined data set will allow us to determine the contributions from the three hypothesized sources: release from the snow, advection from the North Atlantic MBL, or downward mixing from the free troposphere.

...Other Disciplines

Reactive bromine in the free troposphere has a considerable impact on ozone levels and thus on the earth radiation budget. The presence of reactive bromine at Summit opens the question whether the entire on Greenland ice-sheet serves as a bromine source into the free troposphere. Identifying the source of bromine at Summit is crucial to assess the ozone budget in the free troposphere and thus the impact on global climate.

....Human Resource Development

We hope that the experiences and training of the 10 students, the post doc, and the 3 K-12 educators has inspired them, and will serve them well in the future.

....Resources for Research and Education

We hope the interaction with Danish and Greenlandic teachers and students in 2007 will open up possibilities for similar activities in the future, perhaps including seeing some of these students become involved in ongoing research at Summit or elsewhere in Greenland. We are looking forward to another visit by Greenlandic teachers at Summit at the end of our 2008 experiment.

.... Beyond Sci and Eng

nothing to report

Findings

In our first annual report written shortly after the 2007 field season we summarized our preliminary findings as noted below:

- 1) BrO was detected at Summit by both long path DOAS and the low pressure CIMS. Mixing ratios rarely exceeded 3 pptv, but both techniques reported similar values, and a distinct diurnal pattern (sun-synchronous peak) on most days of the campaign.
- 2) Soluble Br⁻ detected by the MC/IC was also above detection limits throughout the campaign, with a diurnal variation from 0.5 – 1.0 pptv up to about 3.0 pptv that was more or less in phase with that of BrO. On 2 days firn air at a depth of 10 cm was sampled, both days the mixing ratios in firn air exceeded those at 1 m above the snow around the time of solar noon, but even in firn air the mixing ratios did not exceed 10 pptv.
- 3) Aerosol bromide was detected in nearly all of the 24 hour filter samples, but the mixing ratios did not exceed 1 pptv. Increasing temperatures in late May and early June appeared correlated with a significant drop in aerosol bromide.
- 4) Mercury showed distinct diurnal changes in speciation that would appear to be consistent with Br chemistry. GEM often decreased at mid-day, while RGM was increasing. Many days the fine particulate Hg peaked in the evening, out of phase with the RGM.
- 5) The HO₂/OH ratio showed a pronounced and repeated daily cycle, with a deep minimum around noon on most days. Model studies to assess whether this pattern is consistent with control by NO_x chemistry, or indicative of Br chemistry, are beginning now.
- 6) NO mixing ratios were lower than we observed in 2003 and 2004 (also lower than those reported by Honrath et al. during the 1998, 1999, and 2000 seasons).

All of these findings have survived closer scrutiny over the past year.

Figure 1 shows an intercomparison of the various bromine measurements during a five day period. Using a typical airmass factor and boundary layer height to convert the MAX-DOAS DSCD's to boundary layer averaged mixing ratios yields similar results to the CIMS observations. The diurnal pattern in the bromine data is clearly visible.

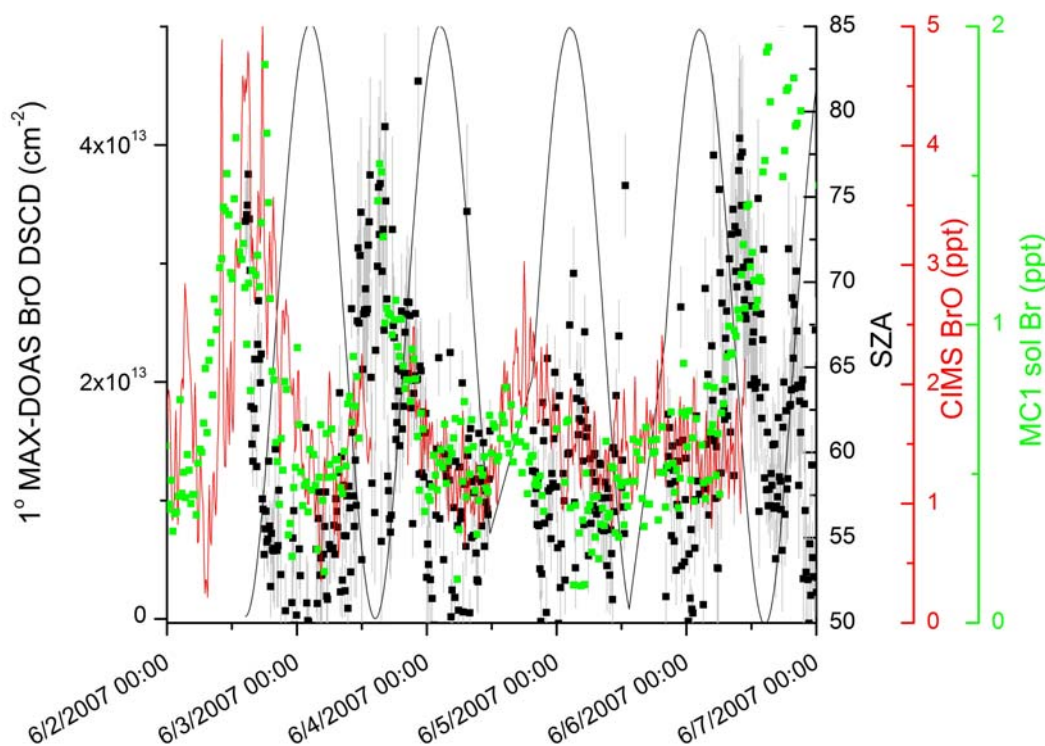


Figure 1: Intercomparison of CIMS BrO mixing ratios (red), MAX-DOAS BrO differential slant column densities (DSCD) (black) and soluble bromide (green).

Preliminary analysis with the 0-D model strongly suggest that the BrO levels are significantly impacting both Hg and HO_x at Summit. As we found in 2003, standard chemistry (not including Br) fails to account for elevated OH observed for periods of hours to several days. In 2007, largest discrepancies between model estimated and observed OH occurred at the same times that RGM was enhanced, and O₃ was modestly depressed (Figure 2). Br is the only oxidant known to be capable of oxidizing GEM to RGM rapidly enough to create the pronounced diurnal variations of RGM we observed. Nighttime minima of RGM suggest that deposition to the snow is a strong sink, and imply an RGM lifetime at Summit during our campaign in the 3-10 hour range. Assuming that a 7-hour lifetime is short enough that RGM production is roughly balanced by deposition allows estimation of Br from the steady state relationship:

$$[\text{Br}] = \frac{[\text{RGM}]}{[\text{GEM}] \cdot k_{\text{Br}+\text{GEM}} \cdot (7\text{hr})}$$

It should be noted that $k_{\text{Br}+\text{GEM}}$ is not well established, determinations reported by *Ariya et al.* (2002) and *Donohoue et al.* (2006) differ by nearly an order of magnitude. Both values were used to estimate Br. The lifetime of BrO at Summit in May-June is on the order of 25 s, allowing BrO to be estimated using the Br constrained by Hg observations and the relationship:

$$\frac{[BrO]}{[Br]} = \frac{k_1[O_3]}{2k_2[BrO] + k_3[HO_2] + k_4[NO] + J_{BrO}}$$

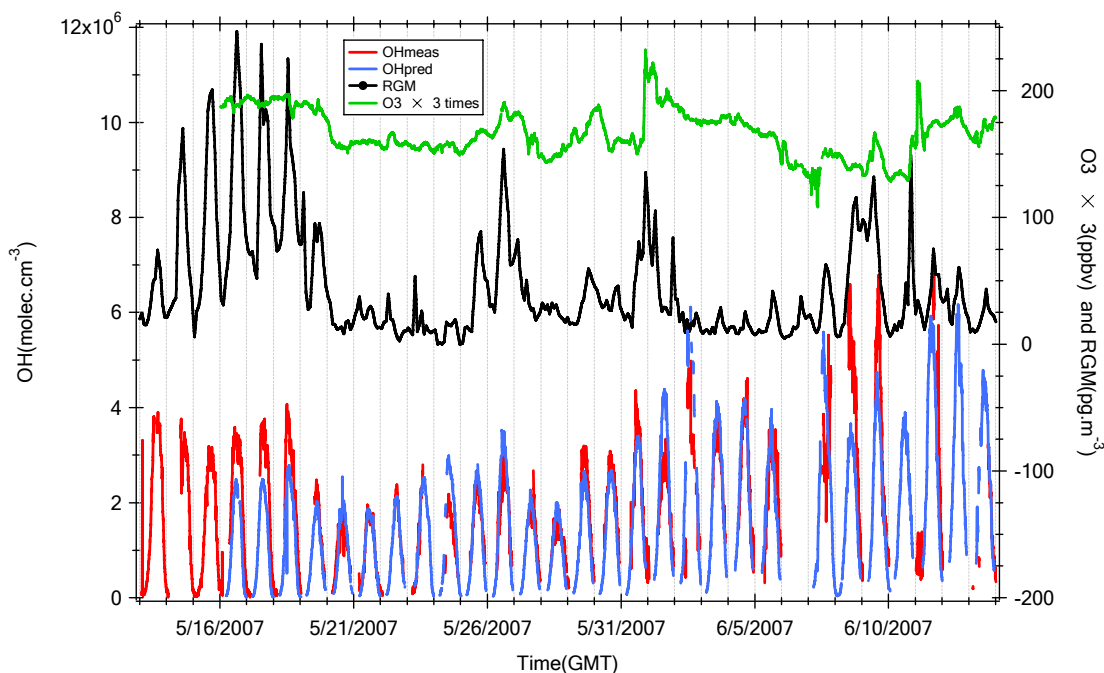


Figure 2. Comparison of OH predictions from the HO_x-NO_x-CH₄ model to OH measurements, plotted with RGM and O₃ concentrations.

Adding Br chemistry into the 0-D model, with Br estimated from Hg as described above leads to marked improvement in the comparison between modeled and observed OH (Figure 3), and also yields estimated BrO levels similar to the CIMS observations (Figures 3 and 4) when the *Donohoue et al.* (2006) rate constant is used. Making the same calculation using the *Ariya et al.* (2002) rate constant suggests much lower levels of Br and BrO that have negligible impact on HO_x cycling under the conditions we observed at Summit.

We realize that the steady state assumption for RGM is tenuous, and introduces large uncertainty into the estimation of Br, hence BrO. In the future our 1D model will allow a more quantitative description of bromine and Hg chemistry.

The combined dataset from the 2007 Summit field campaign indicates that reactive bromine is present at significant levels. Analysis of RGM data with the rate constant for reaction measured by *Donohoue et al.* (2006) and the CIMS observations are consistent with daytime BrO levels of at least 1-2 pptv with periods of up to 5-10 pptv. This is consistent with the persistent low level depletion of ozone in the Summit boundary layer relative to the air above.

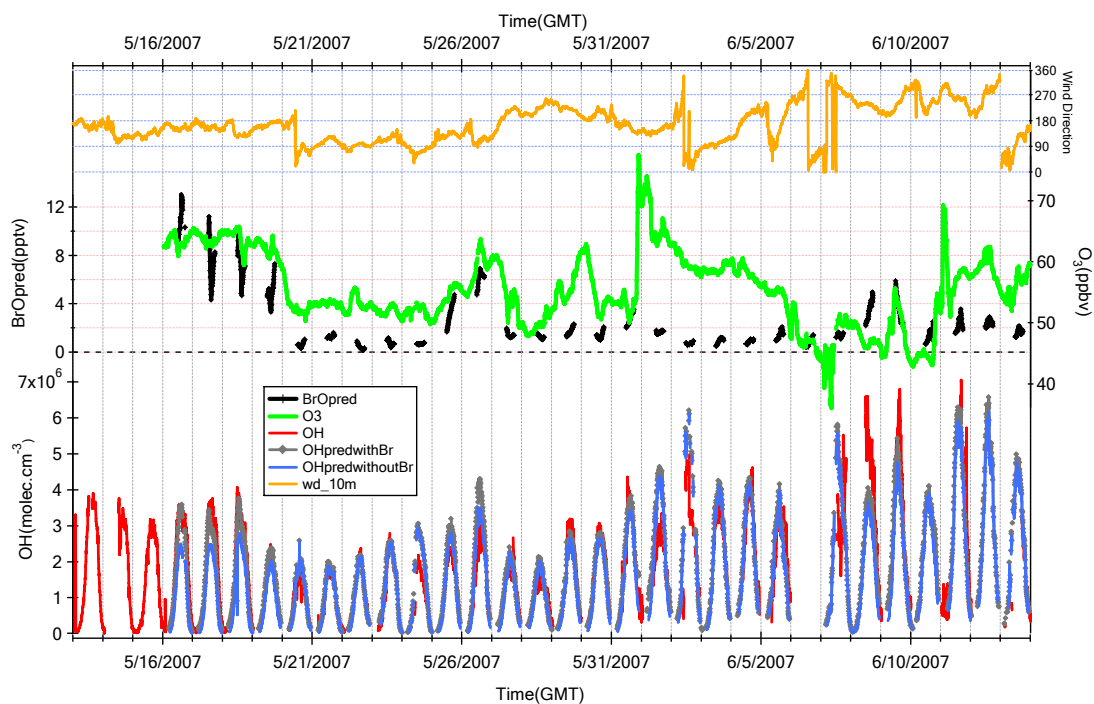


Figure 3. Comparison of OH predictions from the $\text{HO}_x\text{-NO}_x\text{-CH}_4\text{-BrO}_x$ model to OH measurements, plotted with BrO_x predictions, ozone and wind direction at 10 m for the rate constant of *Donohoue et al.*.

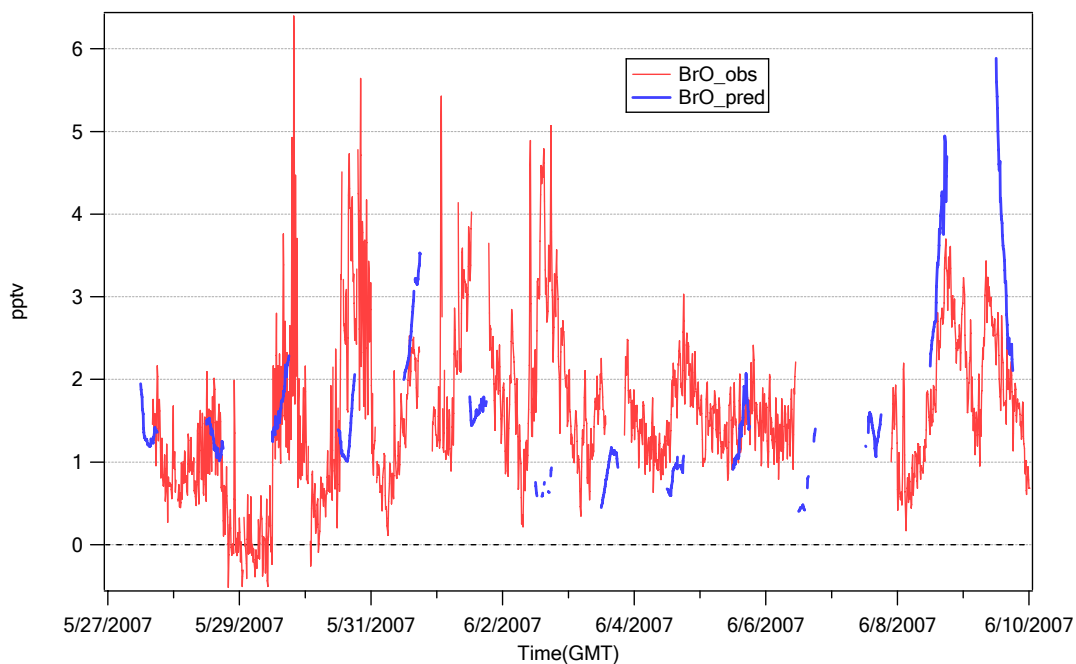


Figure 4. Comparison of the predicted BrO concentrations (using the *Donohoue et al.* rate constant for $\text{Br} + \text{GEM}$) and the observed BrO levels.

Findings

In our first annual report written shortly after the 2007 field season we summarized our preliminary findings as noted below:

- 1) BrO was detected at Summit by both long path DOAS and the low pressure CIMS. Mixing ratios rarely exceeded 3 pptv, but both techniques reported similar values, and a distinct diurnal pattern (sun-synchronous peak) on most days of the campaign (Figure 1).
- 2) Soluble Br⁻ detected by the MC/IC was also above detection limits throughout the campaign, with a diurnal variation from 0.5 – 1.0 pptv up to about 3.0 pptv that was more or less in phase with that of BrO. On 2 days firn air at a depth of 10 cm was sampled, both days the mixing ratios in firn air exceeded those at 1 m above the snow around the time of solar noon, but even in firn air the mixing ratios did not exceed 10 pptv.
- 3) Aerosol bromide was detected in nearly all of the 24 hour filter samples, but the mixing ratios did not exceed 1 pptv. Increasing temperatures in late May and early June appeared correlated with a significant drop in aerosol bromide.
- 4) Mercury showed distinct diurnal changes in speciation that would appear to be consistent with Br chemistry. GEM often decreased at mid-day, while RGM was increasing. Many days the fine particulate Hg peaked in the evening, out of phase with the RGM.
- 5) The HO₂/OH ratio showed a pronounced and repeated daily cycle, with a deep minimum around noon on most days. Model studies to assess whether this pattern is consistent with control by NO_x chemistry, or indicative of Br chemistry, are beginning now.
- 6) NO mixing ratios were lower than we observed in 2003 and 2004 (also lower than those reported by Honrath et al. during the 1998, 1999, and 2000 seasons).

All of the 2007 preliminary findings have survived closer scrutiny, but 2008 provided some surprises.

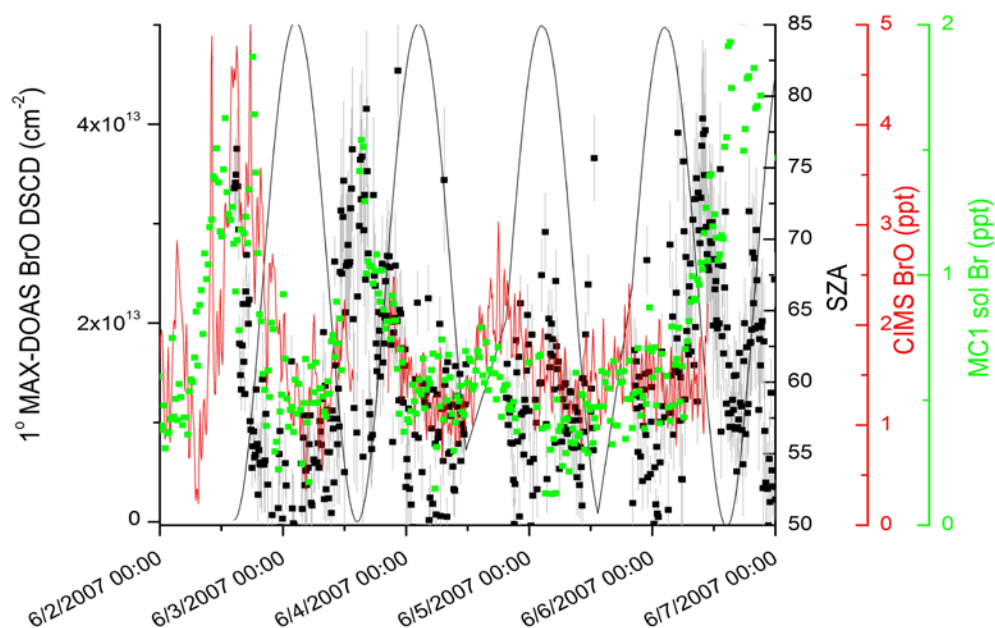


Figure 1: Intercomparison of CIMS BrO mixing ratios (red), MAX-DOAS BrO differential slant column densities (DSCD) (black) and soluble bromide (green) during the 2007 campaign.

Measurements of BrO by long-path DOAS and soluble bromide by the MC/IC technique suggest that bromine compounds were most abundant early in the 2008 season, but decreased to low levels for most of June. Mixing ratios in early June 2008 were comparable to those seen at the end of the 2007 season, thus the 2008 season mean abundance of reactive bromine appeared to be lower than that in 2007 (Figures 2 and 3). However, NMHC ratios suggested that Br chemistry was more active in 2008 than in any previous summer campaign that UCI participated in (Gorham et al., 2008). In addition,

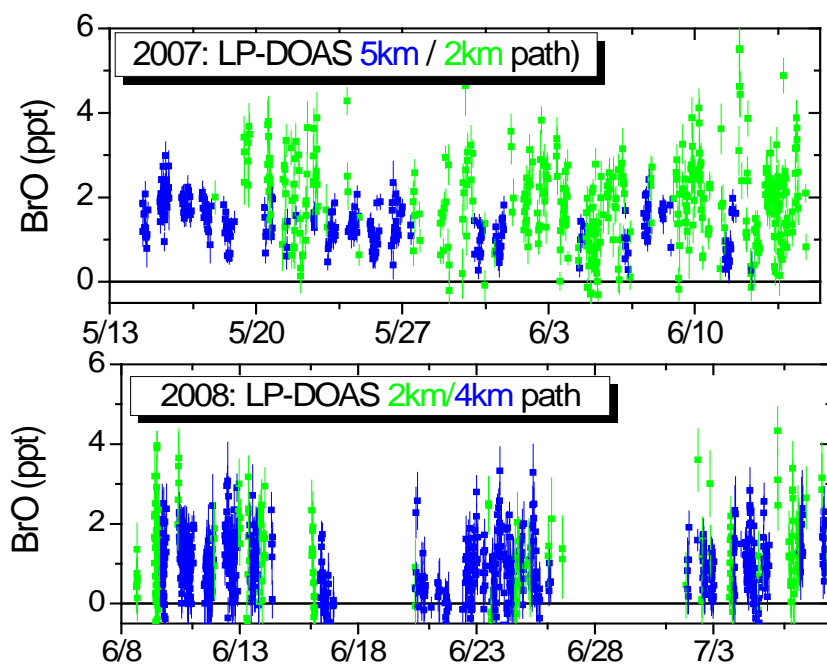
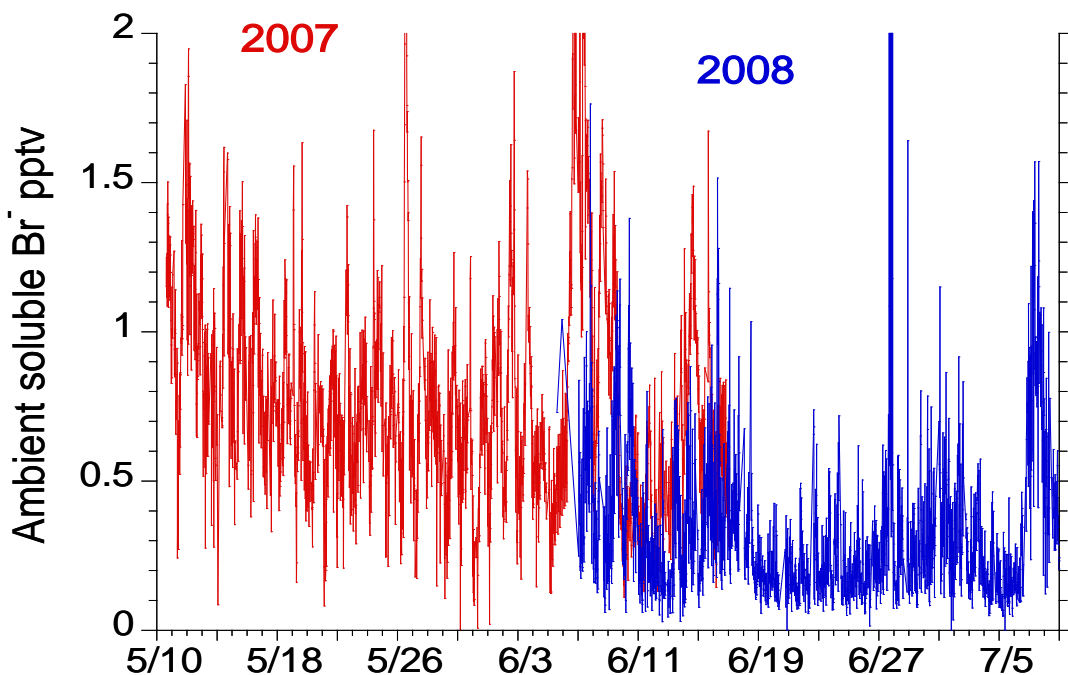


Figure 2. Comparison of BrO mixing ratios measured by long path DOAS in the 2007 and 2008 campaigns at Summit.



Figure

3. Soluble gas phase bromide in the air above the snow at Summit in 2007 and 2008.

while supporting the DOAS evidence for lower average BrO mixing ratios in 2008 than 2007, the CIMS team reported several short (hours long) intervals with enhanced BrO (up to nearly 10 ppt) that were not observed by DOAS (Figure 4). Several of these events occurred shortly after increases in the concentration of bromide in surface snow, and appeared to be related to enhanced downward mixing of upper tropospheric air to the surface.

These discrepancies sparked a lot of discussion at our meetings, and caused most teams to repeatedly recheck all steps in data processing. None of this resulted in major changes in any data sets, so some periods of disagreement remain unresolved. However, we aware that caution will be required when interpreting BrO mixing ratios at low ppt levels from either instrument.

2008

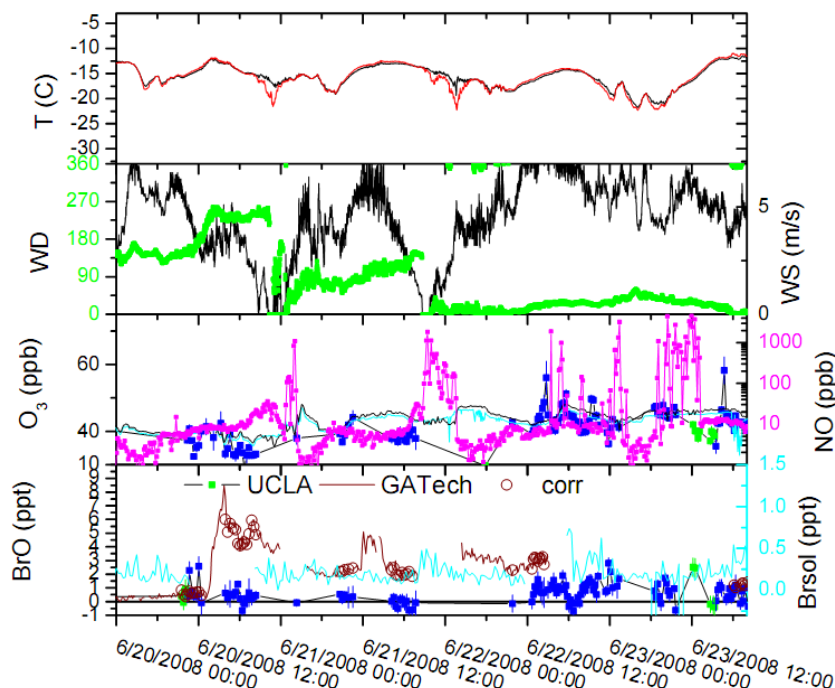


Figure 4. Selected data streams from our 2008 campaign. Note the lower panel in particular: the enhanced BrO reported by CIMS was not observed by long-path DOAS (green for 2km and blue for 4km light path data). Soluble gas phase bromide from MC/IC also shows little enhancement. However, ^{7}Be and meteorologic analyses indicate enhanced downward mixing at this time.

Hg Speciation.

Measurements of elemental and reactive mercury in the

gas phase (GEM and RGM, Respectively) at Summit provided strong indirect evidence for active Br chemistry in 2007. Many days in that season were characterized by a sun-synchronous peak in RGM, usually coinciding with small decreases in GEM (Figure 5, top panel). The only oxidant known to be capable of reacting with GEM rapidly enough to create such enhancements is Br. The radical product HgBr must further react to create RGM (likely HgBrX where X is also a halogen or OH), but the mechanism is not well understood.

Early in the 2008 season (first week of June), similar diurnal variations in RGM were observed. However, later in the season the correlation between RGM and the photolysis of Br_2 broke down, with smaller enhancements in RGM restricted to "nighttime" when the sun was close to the horizon. These observations appear to be explained by the higher air temperatures at Summit in late June and July, since HgBr is thermally unstable (lifetime approximately doubles for 6 C decrease in temperature). Summit's unique characteristics have allowed the competing processes of HgBr production (controlled largely by photolysis of Br_2) and thermal decomposition (controlled by temperature) to be separated. Conversion of GEM to RGM at Summit is only efficient at times when the solar elevation is > 7 degrees and air temperatures are below -15 C. At locations with higher abundances of Br oxides the critical temperature will also be higher due to increased production of HgBr and then HgBrX (Brooks et al., in preparation).

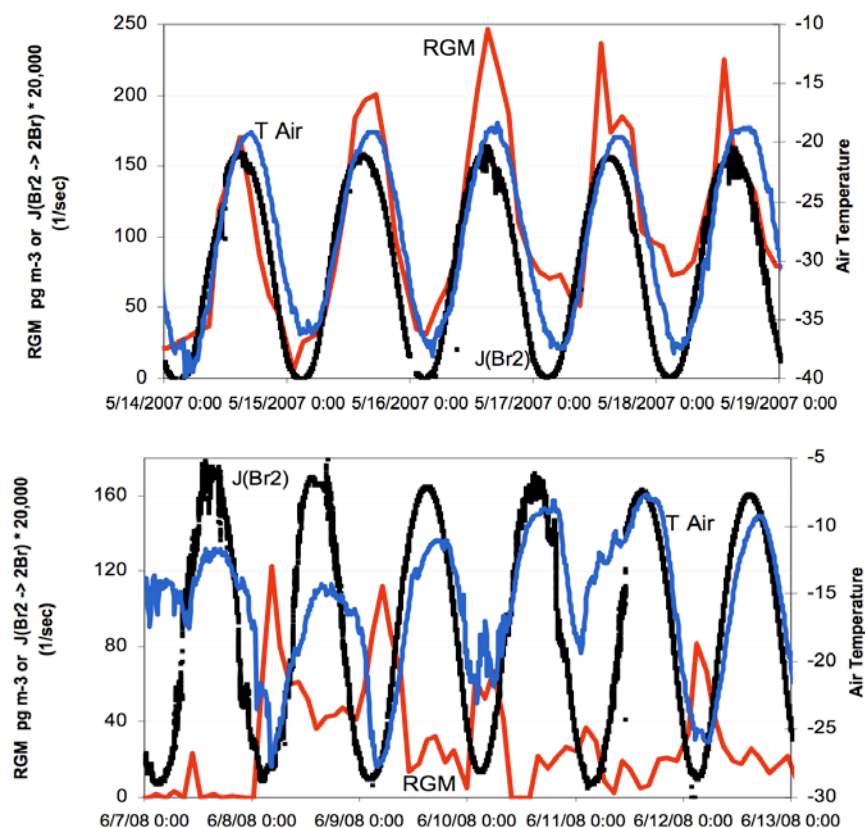


Figure 5. Comparison of the diurnal variation of RGM at Summit early in 2007 (top panel) and later in 2008 (bottom) panel. Temperature and JBr_2 are also shown. When it is cold RGM closely tracks the production of Br by photolysis of Br_2 . In mid summer daytime production of RGM is not significant at temperatures greater than about $-15\text{ }^{\circ}\text{C}$.

MISTRA with New Snow Model.

We have developed a 1-D photochemical model for snow chemistry and integrated it with the MISTRA model (von

Glasow et al., 2002). The MISTRA model is a 1-D boundary layer model including meteorology and chemistry that has historically been used to understand the importance of halogen chemistry in the marine boundary layer and other regions where halogen chemistry is present.

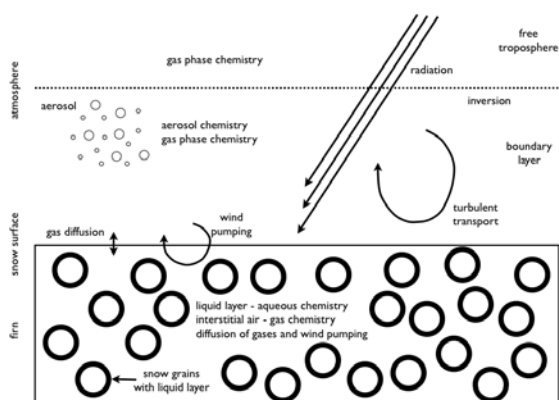


Figure 6. The physical and chemical processes included in the coupled snow-MISTRA model. Gas phase chemistry is calculated in all model layers, aqueous chemistry is calculated in a liquid layer on snow grains. Transport of gas phase species in air and snow is also included. Aerosol chemistry for Summit conditions is not yet included.

The new model for snow includes snow photochemistry, heat transport in the snow pack, diffusion of gases within interstitial air, and wind pumping. The model also includes chemical reactions in

the gas phase and chemistry in a liquid layer on snow grains, with a focus on the cycling of halogen compounds (Figure 6). There is a large amount of uncertainty in the model because the

chemistry of ice surfaces is largely uncharacterized. It is clear that there is a “liquid like” layer on the surface of ice that has similarities to an aqueous solution. We have extrapolated measured aqueous reaction rates to relevant temperatures (at Summit) and supplemented these by including reactions specific to ice surfaces (for nitrate) when measurements are available. Measured concentrations of the bromide, nitrate, and chloride content in melted surface snow (Dibb et al., 2008) have been used to initialize the snow liquid layer in the model.

In order to study halogen chemistry at Summit we must correctly describe boundary layer evolution and the resulting chemical transport in the model. Tethersonde temperature profile measurements taken during 2008 have guided our description of the boundary layer in the model. The modeled meteorology is based on measurements taken on June 10th, 2008, during a period of relatively calm winds and clear conditions. Measurements of snow temperature profiles near the snow surface in 2008 (Helming et al., 2008) have been used to ensure that modeled snow temperatures are consistent with measurements.

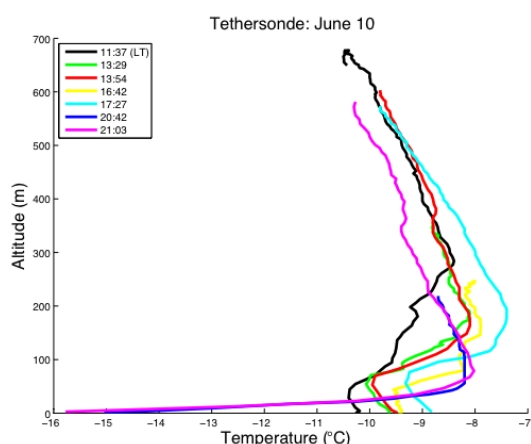
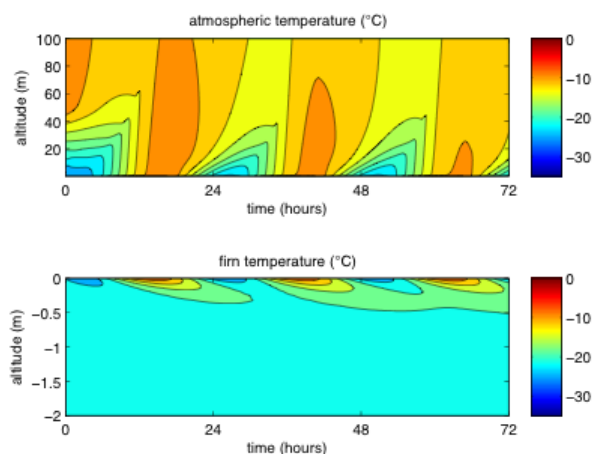


Figure 7. Measured temperature profiles on June 10th, 2008, note the legend refers to local time. The measured profiles show a strong stable inversion at night that breaks up as the snow surface warms during the day (Lefer et al., 2008).

Figure 8. Modeled temperature evolution during a three-day run, note that model time is given in hours starting at midnight local time such that 0, 24, and 48 refer to midnight local time. We define negative altitudes to be a distance below the snow surface ($z=0$). Ensuring the model reproduces the stable inversion observed at night is essential for correctly modeling chemical transport. Preliminary model results show that chemistry on a liquid layer on snow results in BrO and NO release from the snow pack (Figures 9 and 10), leading to mixing ratios of these species similar to those observed at Summit. In addition, ozone destruction in the interstitial air is observed in model runs (not shown). We are currently working to understand if modeled ozone loss in interstitial air is consistent with measurements of interstitial air ozone mixing ratios (for example: Peterson and Honrath, 2001).



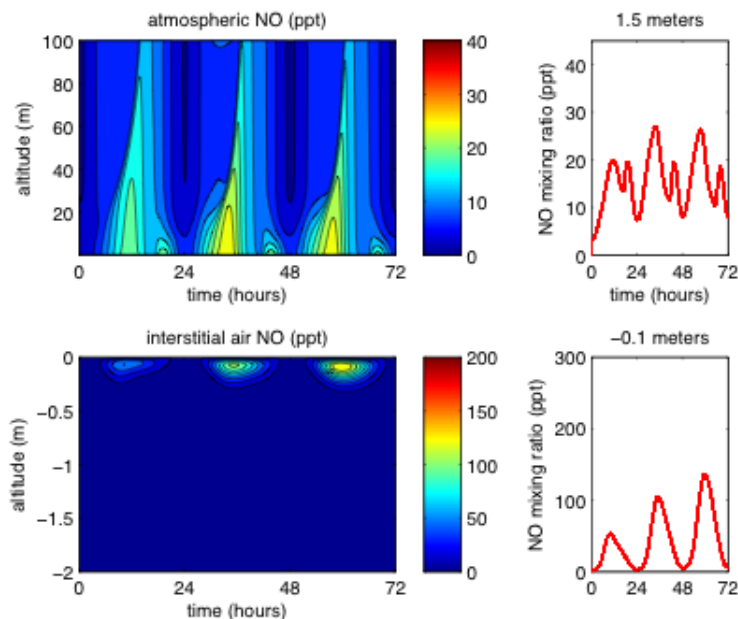


Figure 10. Modeled ambient and interstitial air BrO mixing ratios. Br_2 is produced in the liquid layer on snow grains and is subsequently transferred to interstitial air. BrO is produced from Br_2 photolysis. A variety of bromine compounds including Br_2 and BrO are mixed up into ambient air.

We have made significant strides towards building a 1-D photochemical model for snow in the past year. There are several ongoing projects that are underway to complete our current work modeling snow photochemistry. These include updating the aerosol initialization in the atmosphere to include ambient aerosol in model runs and eventually including mercury chemistry in the model in order to compare with the mercury measurements taken at Summit.

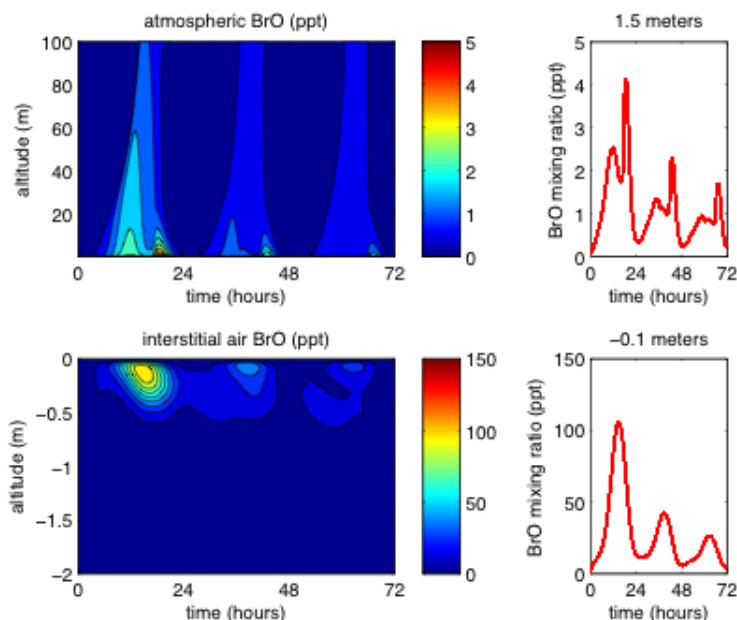


Figure 9. Modeled ambient and interstitial air NO mixing ratios. Snow grains are a source for ambient NO_x (here we only show results for NO, a similar trend is observed for NO_2). NO_x is produced from nitrate photolysis on the surface of snow grains, released into interstitial air, and then mixed upwards into ambient air.